

A Novel Carbons-Adjacent *arachno*-C₂B₁₀ Carborane Tetraanion Bearing both Hexagonal and Pentagonal Bonding Faces

Guofu Zi, Hung-Wing Li, and Zuowei Xie*

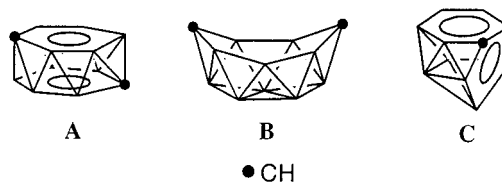
Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

Received June 19, 2001

Summary: A novel carbons-adjacent *arachno*-carborane tetraanion has been prepared and structurally characterized for the first time by direct reduction of 1,2-*o*-xylylene-1,2-carborane with excess Li metal. This tetraanion possesses both hexagonal and pentagonal bonding faces, which would lead to the generation of a new class of metallacarboranes.

It has been well-documented that *o*-R₂C₂B₁₀H₁₀ (R = H, alkyl, aryl) can be reduced by alkali metals to give the “carbons-apart” dianionic species [*nido*-R₂C₂B₁₀H₁₀]²⁻, which are very useful versatile synthons for the production of numerous metallacarboranes of s, p, d, and f elements.¹ This reduction process leads to complete cleavage of the cage C–C bond without exception.² Excess alkali metals cannot directly drive *o*-carborane to *arachno*-carborane.^{1,3} However, in the presence of transition-metal halides *o*-carborane can undergo four-electron reduction to form a *arachno*-R₂C₂B₁₀H₁₀⁴⁻ tetraanion with excess alkali metals.^{4–7} There are two isomers known for the *arachno*-R₂C₂B₁₀H₁₀⁴⁻ tetraanion: one with the proposed geometry of a hexagonal antiprism having two open six-membered faces (**A** in Chart 1)⁴ and the other having a basket shape with one open seven-membered face (**B** in Chart 1).^{5–7} It is noted that two cage carbon atoms are further separated in the *arachno*-R₂C₂B₁₀H₁₀⁴⁻ tetraanion. We have recently found that the two cage carbon atoms remain adjacent in *ortho* positions during the two-electron-reduction process if they are linked by a short bridge.⁸ We have discovered the unprecedented direct reduction of μ -1,2-[*o*-C₆H₄(CH₂)₂]-1,2-C₂B₁₀H₁₀ (**1**) by lithium metal to give

Chart 1. *arachno*-C₂B₁₀H₁₂⁴⁻ Isomers



a novel *arachno*-carborane tetraanion (**C** in Chart 1). This finding is reported herein.

Treatment of **1** with excess finely cut lithium metal in THF at room temperature gave, after workup, the novel *arachno* compound [$\{\mu$ -1,2-[*o*-C₆H₄(CH₂)₂]-1,2-C₂B₁₀H₁₀]₂Li₄(THF)₆ (**2**) as orange crystals in 76% yield.⁹ Recrystallization of **2** from a mixed solvent of DME/THF afforded [$\{\mu$ -1,2-[*o*-C₆H₄(CH₂)₂]-1,2-C₂B₁₀H₁₀]-Li₄(THF)₄(DME)₂ (**3**).⁹ Reaction of **1** with 2 equiv of finely cut lithium metal in THF at room temperature gave a mixture of dianionic and tetraanionic salts on the basis of ¹¹B NMR spectroscopic analyses. Further reaction with excess Li metal generated the single product of **2**. This is the first example reported in the literature that Li metal can directly reduce *o*-carborane to a *arachno*-carborane tetraanion. In sharp contrast, interaction between **1** and excess finely cut sodium metal in THF at room temperature gave, after workup, the “carbons-adjacent” *nido* compound [$\{\mu$ -1,2-[*o*-C₆H₄(CH₂)₂]-1,2-C₂B₁₀H₁₀]₂Na₄(THF)₆ (**4**) as colorless crystals in 69% yield.⁹ No *arachno* species was detected by ¹¹B NMR. **4**, however, could react with excess Li metal in THF to afford **2** after recrystallization. These results may be due to the difference in reducing power of lithium (*E*^o = 3.040 V) and sodium (*E*^o = 2.714 V).¹⁰ It is reasonable to suggest that the lithium analogue of **4** may serve as an intermediate for the formation of **2**. Compounds **2–4** were fully characterized by various spectroscopic data, elemental analyses, and X-ray diffraction studies.^{9,11} All these transformations are outlined in Scheme 1.

The ¹H NMR spectra show the ratio of six THF molecules per carboranyl ligand for **2**, four THF molecules and one DME molecule per carboranyl ligand for **3**, and three THF molecules per carboranyl ligand for

* To whom correspondence should be addressed. Fax: (852) 26035057. Tel: (852)26096269. E-mail: zxie@cuhk.edu.hk.

(1) For recent reviews, see: (a) Saxena, A. K.; Maguire, J. A.; Hosmane, N. S. *Chem. Rev.* **1997**, *97*, 2421. (b) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081. (c) Grimes, R. N. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 1, p 373.

(2) Reaction of 1-Me-1,2-C₂B₁₀H₁₁ with 2 equiv of Co(PEt₃)₄ gave (MeC₂B₁₀H₁₁)Co₂(PEt₃)₃, in which the cage C–C connectivity was believed to be maintained. This compound was subjected to X-ray analysis. However, the nonmethylated cage carbon atom was not definitely identified; see: Barker, G. K.; Garcia, M. P.; Green, M.; Stone, F. G. A.; Welch, A. J. *Chem. Commun.* **1983**, 137.

(3) Chui, K.; Li, H.-W.; Xie, Z. *Organometallics* **2000**, *19*, 5447.

(4) Evans, W. J.; Hawthorne, M. F. *Chem. Commun.* **1974**, 38.

(5) Xie, Z.; Yan, C.; Yang, Q.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 1761.

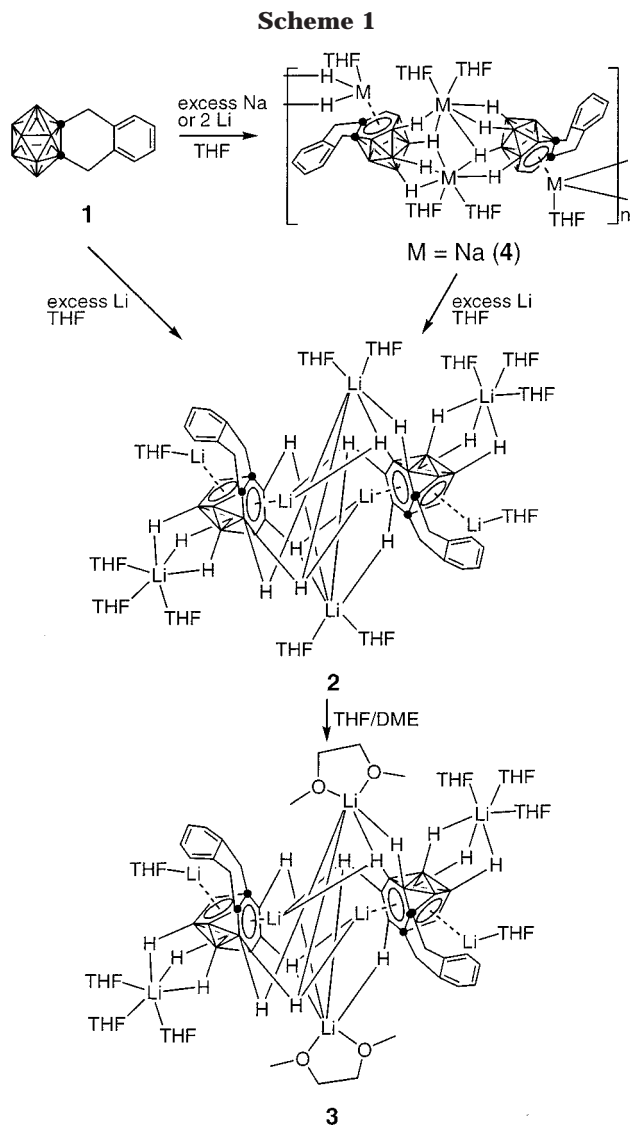
(6) (a) Xie, Z.; Chui, K.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 3947. (b) Chui, K.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2000**, *19*, 1391.

(7) Chui, K.; Yang, Q.; Mak, T. C. W.; Lam, W.-H.; Lin, Z.; Xie, Z. *J. Am. Chem. Soc.* **2000**, *122*, 5758.

(8) Zi, G.; Li, H.-W.; Xie, Z. *Chem. Commun.* **2001**, 1110.

(9) See the Supporting Information for complete experimental procedures and compound characterization data.

(10) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins College: New York, 1993; p A-35.



4, respectively. The ^{11}B NMR spectra exhibit a 2:2:2:1:3 splitting pattern for both **2** and **3** and a 2:2:1:2:1:1:1 splitting pattern for **4**, respectively. The completion of the reduction reactions can be closely monitored by ^{11}B NMR spectroscopy. Their solid-state IR spectra display both a characteristic doublet centered around 2450 cm^{-1} and a shoulder at about 2310 cm^{-1} attributable to an M–H–B stretching mode.^{12,13}

(11) Crystal data for **2** ($\text{C}_{34}\text{H}_{66}\text{B}_{10}\text{Li}_4\text{O}_6$; fw, 706.7): triclinic, space group $P\bar{1}$, $a = 11.922(8)\text{ \AA}$, $b = 12.742(8)\text{ \AA}$, $c = 14.538(10)\text{ \AA}$, $\alpha = 88.42(2)^\circ$, $\beta = 89.10(2)^\circ$, $\gamma = 86.10(2)^\circ$, $V = 2202(2)\text{ \AA}^3$, $T = 293\text{ K}$, $Z = 2$, $d_{\text{calcd}} = 1.066\text{ g/cm}^3$, $R_1 = 0.086$ ($I > 2.0\sigma(I)$), $wR_2(F^2) = 0.242$. Crystal data for **3** ($\text{C}_{30}\text{H}_{60}\text{B}_{10}\text{Li}_4\text{O}_6$; fw, 652.6): triclinic, space group $P\bar{1}$, $a = 14.429(3)\text{ \AA}$, $b = 12.784(3)\text{ \AA}$, $c = 14.486(4)\text{ \AA}$, $\alpha = 69.77(1)^\circ$, $\beta = 79.78(1)^\circ$, $\gamma = 86.33(1)^\circ$, $V = 1954.4(8)\text{ \AA}^3$, $T = 293\text{ K}$, $Z = 2$, $d_{\text{calcd}} = 1.109\text{ g/cm}^3$, $R_1 = 0.077$ ($I > 2.0\sigma(I)$), $wR_2(F^2) = 0.202$. Crystal data for **4** ($\text{C}_{22}\text{H}_{42}\text{B}_{10}\text{Na}_2\text{O}_3$; fw, 508.6): triclinic, space group $P\bar{1}$, $a = 11.767(2)\text{ \AA}$, $b = 11.782(2)\text{ \AA}$, $c = 12.420(2)\text{ \AA}$, $\alpha = 103.81(1)^\circ$, $\beta = 90.04(1)^\circ$, $\gamma = 116.46(1)^\circ$, $V = 1485.6(4)\text{ \AA}^3$, $T = 293\text{ K}$, $Z = 2$, $d_{\text{calcd}} = 1.137\text{ g/cm}^3$, $R_1 = 0.068$ ($I > 2.0\sigma(I)$), $wR_2(F^2) = 0.168$.

(12) (a) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *29*, 2191. (b) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 4962.

(13) (a) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Xue, F.; Mak, T. C. W. *Organometallics* **1998**, *17*, 489. (b) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **1998**, *17*, 1907. (c) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1641. (d) Xie, Z.; Wang, S.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 2420. (e) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **1999**, *18*, 1578. (f) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2000**, *19*, 334.

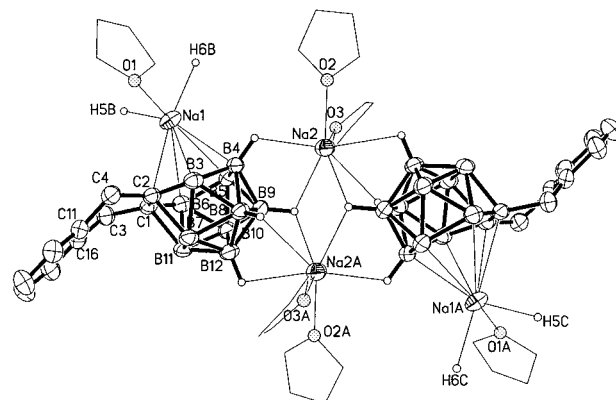


Figure 1. ORTEP view of **4**, showing one asymmetric unit of the infinite polymeric chain (thermal ellipsoids drawn at the 35% probability level).

The common structural feature for all three compounds, as evidenced by X-ray analyses, is that the cage carbon atom adjacency of the precursor is maintained in the product. It is very clear that the short bridge between the two cage carbon atoms can force the carbon atoms to be in *ortho* positions during the reduction process, which differs significantly from the reported positions.^{1,3–7}

Compound **4** adopts a polymeric structure in which the sodium and *nido*-carborane serve as alternating bridging groups to give a zigzag metallacarborane–Na–metallacarborane–Na chain that is maintained in one dimension throughout the lattice. Each asymmetric unit consists of two $\{\mu\text{-}1,2\text{-}[\sigma\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}\text{Na}_2(\text{THF})_3$ structural motifs that are related to each other by an inversion center (Figure 1). One sodium is η^6 -bound to the open six-membered C_2B_4 face and coordinated to one THF molecule and one neighboring *nido*-carborane via two B–H–Na bonds. The other is bonded to a trigonal B_3 face through three B–H–Na bonds and to the neighboring *nido*-carborane via two B–H–Na bonds and coordinated to two THF molecules. The average Na(1)–cage atom and Na(2)–B(H) distances of 2.854(4) and 3.026(4) Å are comparable to the corresponding values found in *closo-exo*- $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{-B}_{10}\text{H}_{10}]\text{Na}_2(\text{THF})_3$ and $[\text{closo-exo}\{(\text{Me}_3\text{Si})_2\text{C}_2\text{B}_4\text{H}_4\}]\text{Na}_2(\text{THF})_4$,¹⁴ respectively.

Both **2** and **3** are centrosymmetric dimers. Their solid-state structures are very similar to each other except for the coordinating solvents around Li(2): THF in **2** and DME in **3**, shown in Figure 2. The *arachno*-carborane consists of one open six-membered C_2B_4 face and one open five-membered C_2B_3 face that are bonded to two lithium atoms in η^6 and η^5 fashions, respectively, to form a novel 14-vertex *closo*-metallacarborane. These two open faces share one common edge of C(1)–C(2). Careful examination of the molecular structures of **3** and **4** indicates that the open five-membered face is generated by breaking the B(7)–B(11) connectivity of the *nido*-carborane in **4** via two-electron uptake from lithium. This is a new isomer of the *arachno*- $\text{R}_2\text{C}_2\text{B}_{10}\text{-H}_{10}^{4-}$ tetraanion and represents the first example of cage C–C connectivity remaining intact after reduction of an *o*-carborane by excess alkali metal.

(14) Hosmane, N. S.; Jia, L.; Zhang, H.; Bausch, J. W.; Prakash, G. K. S.; Williams, R. E.; Onak, T. P. *Inorg. Chem.* **1991**, *30*, 3793.

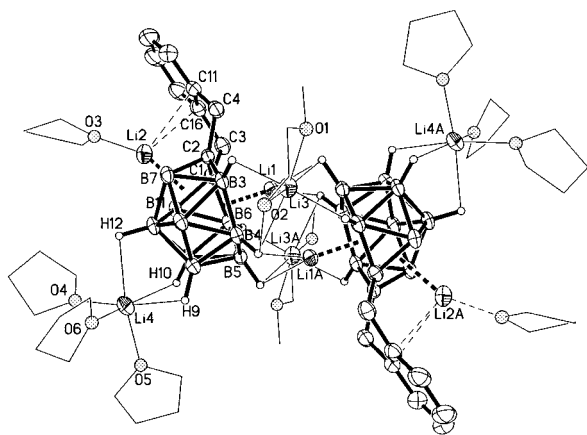


Figure 2. ORTEP view of **3** (thermal ellipsoids drawn at the 35% probability level).

The average Li(1)–cage atom and Li(2)–cage atom distances of 2.315(8) and 2.309(10) Å in **2** are very close to the corresponding values of 2.300(5) and 2.301(5) Å in **3**. These measured values can be compared to the 2.332(9) Å in *closo-exo*-{(Me₃Si)₂C₂B₄H₄}Li₂(TMEDA)₂^{15a} and 2.45(2) Å in [*closo*-{(Me₃Si)₂C₂B₄H₅}₂Li]⁻.^{15b} It is noted that the Li(2)–B(12) distances of 2.572(10) Å in **2** and 2.580(5) Å in **3** are significantly longer than other

(15) (a) Hosmane, N. S.; Saxena, A. K.; Barreto, R. D.; Zhang, H.; Maguire, J. A.; Jia, L.; Wang, Y.; Oki, A. R.; Grover, K. V.; Whitten, S. J.; Dawson, K.; Tolle, M. A.; Siriwardane, U.; Demissie, T.; Fagner, J. S. *Organometallics* **1993**, *12*, 3001. (b) Hosmane, N. S.; Yang, J.; Zhang, H.; Maguire, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 5150.

Li–cage atom distances due to the larger out-of-plane (C(1)C(2)B(7)B(11)) displacement of B(12): 0.60 Å in **2** and 0.61 Å in **3**, respectively. The weak interactions between Li(2) and C(11) and C(16) (2.595(9)–2.660(6) Å) lead to smaller angles of C(1)–C(3)–C(16) and C(2)–C(4)–C(11) (110.4(4)–112.6(2)°) compared to the corresponding values (114.6(3)–114.9(3)°) in **4**, and the shorter Li(2)–C distance is associated with the smaller C–C–C angle.

In summary, a short bridge between two cage carbon atoms of an *o*-carborane can indeed force the two cage carbon atoms to remain adjacent in *ortho* positions during the reduction process, leading to the formation of a novel “carbons-adjacent” *arachno*-carborane tetra-anion. Like other group 1 metallocarboranes, these alkali-metal salts are expected to be useful synthons for the synthesis of metallocarboranes of p, d, and f elements, which may result in a novel class of metallocarboranes.

Acknowledgment. The work described in this paper was supported by a grant from the Research Grants Council of the Hong Kong Special Administration Region (Project No. CUHK 4267/00P).

Supporting Information Available: Complete details for experimental procedures, characterization data, and crystallographic studies of **2**–**4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0105324